Electronic and Rovibrational Quantum Chemical Analysis of C_3P^-: The Next Interstellar Anion?

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ABSTRACT

C_3P^- is analogous to the known interstellar anion C_3N^- with phosphorus replacing the nitrogen in a simple step down the periodic table. In this work, it is shown that C_3P^- is likely to possess a dipole-bound excited state. It has been hypothesized and observationally supported that dipole-bound excited states are an avenue through which anions could be formed in the interstellar medium. Additionally, C_3P^- has a valence excited state that may lead to further stabilization of this molecule, and C_3P^- has a larger dipole moment than neutral C_3P (~ 6 D vs. ~ 4 D). As such, C_3P^- is probably a more detectable astromolecule than even its corresponding neutral radical. Highly-accurate quantum chemical quartic force fields are also applied to C_3P^- and its singly ^{13}C substituted isotopologues in order to provide structures, vibrational frequencies, and spectroscopic constants that may aid in its detection.

1 INTRODUCTION

It is currently uncertain as to why anions are found in the interstellar medium (ISM) with six known to date: C_4H^-, C_6H^-, C_8H^-, CN^-, C_3N^-, and C_5N^- (Cernicharo et al. 2007; Brünken et al. 2007; Remijan et al. 2007; Thaddeus et al. 2008; Cernicharo et al. 2008; Agúndez et al. 2010; Cordiner et al. 2011). Since all of the known anions are closed-shell and, as a result, valence in nature, one of the leading theories about their existence comes from the presence of a dipole-bound excited state (Agúndez et al. 2008). If a neutral molecule possesses a large enough dipole moment (somewhere in excess of $2.0-2.5$ D), it can bind an additional electron in a highly diffuse s-type orbital (Fermi & Teller 1947; Coulson & Walmsley 1967; Gutsev & Adamowicz 1995b,a; Compton et al. 1996; Jordan & Wang 2003; Simons 2008, 2011). These loosely bound excited states (Hammer et al. 2003) can relax to a lower energy valence state if the molecule can support the additional electron in its valence electron cloud. This phenomenon is known for some small anions (Lykke et al. 1987; Mullin et al. 1992, 1993), and its reverse for electronic excitation has even been hypothesized as a potential explanation (Sarre 2000; Cordiner & Sarre 2007; Fortenberry, Crawford & Lee 2013) for at least one of the diffuse interstellar bands, the series of visible to near-infrared absorption features largely uniformly observed towards many stellar objects (Sarre 2006) whose carriers

have only very recently come into focus (Campbell et al. 2015). As such, it is currently hypothesized that the large dipole moment of the neutral-radical captures an incident electron whereby the dipole-bound anion then decays down to the stable, valence ground electronic state (Agúndez et al. 2008; Fortenberry et al. 2013a).

All of the known interstellar anions possess large enough dipole moments to undergo this process save for CN^- which is likely formed by collisional or chemical processes (Larsson, Geppert & Nyman 2012; Carelli et al. 2014). The greater $[C_6H^-]/[C_6H]$ ratio as compared to the significantly smaller $[C_4H^-]/[C_4H]$ ratio is most elegantly explained by the dipole-bound formation hypothesis (Agúndez et al. 2008) especially since C_4H is more abundant than C_6H, but C_6H^- is more abundant than C_4H^-. C_4H must be excited into its low-lying $^2\Pi$ excited state in order to have a dipole moment large enough to capture the additional electron. C_6H is $^2\Pi$ and strongly dipolar in its ground state meaning that capture of the dipole-bound electron is much more likely for the longer hydrocarbon chain. Additionally, C_2H^- has not been detected. Its corresponding neutral-radical is very abundant (Heikkilä, Johansson & Olofsson 1999), but the dipole moment of the unchanged species is not large enough to support a dipole-bound state. Finally, all of the corresponding neutral-radicals are known to exist in the ISM for each of the closed-shell anions detected (McCarthy & Thaddeus 2001).

However, no new anions have been detected in the

ISM since 2010 as reported in the literature (Agúndez et al. 2010). Several candidate anions have been studied quantum chemically in order to provide accurate predictions of their rovibrational nature. These include CH_2CN^-, c- and l-C_3H^-, and $CCOH^-$ (Fortenberry, Crawford & Lee 2013; Fortenberry et al. 2013a, 2014a; Fortenberry & Lee 2015). Another tantalizing potential interstellar anion is C_3P^-. It is analogous with the known C_3N^- anion, and several phosphorus-containing carbon chains (CP, HCP, and CCP) have been detected in the ISM (Guélin et al. 1990; Agúdez, Cernicharo & Guélin 2007; Halfen, Clouthier & Ziurys 2008). However, little is known about l-C_3P^-. The linear neutral-radical is known to be the lowest energy isomer on the [C,C,C,P] potential energy surface and has a strongly dipolar (3.797 D) $^2\Pi$ ground state (del Río, Barrientos & Largo 1996; Maclean et al. 2008). Hence, this present work sets to provide both electronic as well as high-level rovibrational data on C_3P^- in order to assist in its potential detection.

Quantum chemical studies of excited states of anions have recently shown that many anions may possess dipole-bound excited states, and some anion excited states may also be valence in nature (Fortenberry & Crawford 2011b,a; Fortenberry 2013; Fortenberry, Morgan & Enyard 2014; Fortenberry 2014; Theis et al. 2015). Excited states of anions have been experimentally known for many species (Lykke et al. 1987; Mullin et al. 1992, 1993; Grutter, Wyss & Maier 1999; Pachkov et al. 2001; Pino et al. 2002, 2004), but the number of dipole-bound excited state candidate anions has increased with the improvement of computational tools. Additionally, high-level rovibrational computations have been able to produce rotational constants to within 15 MHz of experiment and vibrational frequencies to within 1.0 cm^{-1} of laboratory results in some cases (Huang, Taylor & Lee 2011; Inostroza, Huang & Lee 2011; Fortenberry et al. 2012b,a; Huang, Fortenberry & Lee 2013a; Zhao, Doney & Linnartz 2014; Fortenberry et al. 2014b). Consequently, both approaches are applied to C_3P^- in this work in order to elucidate more fully the chemical physics of this potentially astrochemically significant anion.

2 COMPUTATIONAL DETAILS

All computations make use of coupled cluster theory at either the singles and doubles (CCSD) or singles, doubles, and perturbative triples [CCSD(T)] levels (Raghavachari et al. 1989; Crawford & Schaefer III 2000; Shavitt & Bartlett 2009) and the correlation-consistent family of basis sets in the cc-pVXZ from (Dunning 1989; Peterson & Dunning 1995; Kendall, Dunning & Harrison 1992). The cc-pV(X+d)Z basis sets are used for the phosphorus atom, but this distinction should be understood by the reader to be implied for the remainder of the discussion. Additionally, restricted Hartree-Fock reference wavefunctions (Scheiner et al. 1987) and the PSI4 quantum chemistry software (Turney et al. 2012) are utilized except where noted.

The electronically excited states are computed vertically using the equation of motion (EOM) formalism (Stanton & Bartlett 1993; Krylov 2007) of CCSD and are based on the optimized CCSD(T)/aug-cc-pVTZ geometry. Increasing the diffuseness of the basis set allows one to observe the convergence of the excitation energy. Early convergence in the series indicates a valence excited state while late convergence is a sign that the excited state of interest is dipole-bound. This can them be corroborated by analysis of the orbitals involved from the most diffuse basis set. The double-zeta (n-aug-cc-pVDZ where $n = 0 - 3$) and triple zeta (m-aug-cc-pVTZ where $m = 0 - 2$) basis sets are employed. The vertical electron binding energy (eBE), the energy required to removed the electron from the system starting from the ground electronic state, is computed using the ionization potential form of EOM: EOMIP-CCSD (Stanton & Gauss 1994).

The rovibrational computations utilize the scheme developed previously (Huang & Lee 2008, 2009; Huang, Taylor & Lee 2011) that has met with much success as described above. The optimized CCSD(T)/aug-cc-pV5Z geometry is corrected for core-electron inclusion by adding the differences in the bond lengths between the CCSD(T) computations utilizing the Martin-Taylor (MT) core correlating basis set (Martin & Taylor 1994) with and without inclusion of the core electrons: $1s$ for carbon and $1s$, $2s$, and $2p$ for phosphorus. From this reference geometry, a quartic force field (QFF) is constructed. A QFF is fourth-order Taylor series expansion of the potential portion of the nuclear Hamiltonian (Fortenberry et al. 2013b). It takes the form:

$$V = \frac{1}{2}\sum_{ij}F_{ij}\Delta_i\Delta_j + \frac{1}{6}\sum_{ijk}F_{ijk}\Delta_i\Delta_j\Delta_k + \frac{1}{24}\sum_{ijkl}F_{ijkl}\Delta_i\Delta_j\Delta_k\Delta_l, \tag{1}$$

where Δ_i are displacements and $F_{ij...}$ are the force constants. The displacements are defined from C_1 as the terminal carbon atom opposite the phosphorus:

$$S_1(\Sigma^+) = C_1 - C_2 \tag{2}$$
$$S_2(\Sigma^+) = C_2 - C_3 \tag{3}$$
$$S_3(\Sigma^+) = C_3 - P \tag{4}$$
$$S_4(\Pi_{xz}) = \angle C_1 - C_2 - C_3 - \mathbf{y} \tag{5}$$
$$S_5(\Pi_{xz}) = \angle C_2 - C_3 - P - \mathbf{y} \tag{6}$$
$$S_6(\Pi_{yz}) = \angle C_1 - C_2 - C_3 - \mathbf{x} \tag{7}$$
$$S_7(\Pi_{yz}) = \angle C_2 - C_3 - P - \mathbf{x}. \tag{8}$$

A similar coordinate setup has been utilized previously on the structurally-related l-C_3H^+ cation (Huang, Fortenberry & Lee 2013b). The step sizes for the bond length displacements are 0.005 Å and 0.005 radians for the bends.

625 total displacements are needed to describe the C_3P^- QFF. At each displacement, seven quantum chemical computations are undertaken at the CCSD(T) level. Extrapolation of the aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z energies to the complete basis set (CBS) limit via a three-point formula (Martin & Lee 1996) provides the reference energy for each point. Differences between the MT computed energies including and not including core electrons are added to the CBS energy. Furthermore, Douglas-Kroll scalar relativistic corrections (Douglas & Kroll 1974) available in the MOLPRO 2010.1 quantum chemistry program (Werner et al. 2010) are also added to the CBS en-

ergy. The CcCR QFF (Fortenberry et al. 2011) is created from this approach where the CBS energy ("C"), core correlation ("cC"), and relativistic terms ("R") provide for a very detailed description of the molecular potential energy surface.

The energy points are fitted to the force constants via a least-squares formula. Refitting the surface provides the CcCR minimum equilibrium geometry as well as the proper force constants including zero value gradients. Transformation of the force constants into Cartesian coordinates is accomplished via the INTDER (Allen & coworkers 2005) program. Rotational (Mills 1972; Watson 1977) and vibrational (Papousek & Aliev 1982) perturbation theory computations at second order (VPT2) produce spectroscopic constants and anharmonic vibrational frequencies, respectively, through the SPECTRO program (Gaw et al. 1991). A $2\nu_3 = \nu_2$ type-1 Fermi resonance is included in SPECTRO's VPT2 computations. Møller-Plesset second-order electronic perturbation theory (MP2) computations with the 6-31+G* basis set (Møller & Plesset 1934; Hehre, Ditchfeld & Pople 1972) in the Gaussian09 program (Frisch et al. 2009) provide the vibrational intensities.

3 RESULTS AND DISCUSSION

3.1 Vertical Electronically Excited States

The ground electronic state C_3P has a $\tilde{X}\ ^2\Pi$ term and a $(core)7\sigma^2 8\sigma^2 9\sigma^2 10\sigma^2 2\pi^4 11\sigma^2 3\pi^3$ electronic configuration (del Río, Barrientos & Largo 1996). The anion's additional electron occupies the 3π orbital to complete the shell and give a valence $\tilde{X}\ ^1\Sigma^+$ ground state term. The 3π highest occupied molecular orbital (HOMO) is significant for the electronic properties of the anion. Computations of the first two vertically excited states of C_3P^- are given in Table 1. Both excitations are out of the 3π HOMO. The $2\ ^1\Sigma^+$ state involves excitations into the $4\pi^*$ orbital, while the $1\ ^1\Pi$ state is produced by exciting the electron into a diffuse s-type orbital.

The $1\ ^1\Pi$ state is a candidate for classification as a dipole-bound excited state. The excitation energy decreases significantly as the spatial extent of the orbitals increases, the excitations are, again, into high-diffuse orbitals as is necessary for a dipole-bound state (Skurski, Gutowski & Simons 2000; Morgan & Fortenberry 2015), and the eBE and dipole-bound excitation energy are nearly coincident. Since the eBEs of dipole-bound states are known to be on the order of ~ 0.01 eV (Hammer et al. 2003; Diken, Hammer & Johnson 2004), the latter point is a clear marker of dipole-bound behavior. Additionally, the dipole moment of the $C_3P\ \tilde{X}\ ^2\Pi$ state at the anion geometry is computed here by CCSD(T)/aug-cc-pVTZ to be 4.20 D, in line with previous computations (Maclean et al. 2008) and large enough to support a dipole-bound state.

The $2\ ^1\Sigma^+$ state is actually valence. Its excitation is not affected by the increase in the diffuseness of the basis set and is well-below the eBE. It is the product of a $\pi \to \pi^*$ excitation which is similar to π electron systems in polyunsaturated carbon chains, a commonly-used application of the particle-in-a-box quantum mechanical model system. Hence, C_5P^- and longer chains of this family will also likely possess

a valence excited state. The $C_3P^-\ 2\ ^1\Sigma^+$ excitation energy is well converged to the 3.30 eV level for the double-zeta bases and similarly at 3.24 eV for the triple-zeta bases.

Even though the intensities for the transitions are very small, C_3P^- is still an excellent candidate for dipole-bound, gas phase synthesis starting from the neutral-radical in the ISM or in circumstellar media. Capture of the electron by the neutral radical can proceed through the dipole-bound excited state producing the valence, closed-shell anion. The valence excited state provides an additional avenue for energy dissipation. This may likely increase its interstellar lifetime giving an exceptionally high $[C_3P^-]/[C_3P]$ ratio, potentially greater than that observed for $[C_6H^-]/[C_6H]$. As a result, C_3P^- should be more readily observed than its corresponding neutral radical since its electronic properties are more enhanced than the other known interstellar anions. In order to detect C_3P^-, information regarding the $\tilde{X}^1\Sigma^+$ valence ground electronic state's rotational, vibrational, and rovibrational behavior is needed and provided here for the first time from further quantum chemical computations.

3.2 Rovibrational Analysis

The fitting of the force constants needed to define the CcCR QFF and produce the subsequent spectroscopic data of ground state $\tilde{X}^1\Sigma^+\ C_3P^-$ is very tight with a sum of residuals squared on the order of 10^{-16} a.u.^{2} The force constants for l-C_3P^- are given in Table 2 and follow the coordinate labeling given above. For instance, F_{11} corresponds to the second-derivative of the C_1-C_2 bond. Additionally, the harmonic, diagonal force constants are proportional to the bond strengths. F_{11} is the largest of these indicating that the C_1-C_2 bond is the strongest. This is corroborated by the R_α vibrationally averaged bond lengths given in Table 3. The $r_0(C_1-C_2)$ value is 1.259 055 Å, the shortest bond length given indicating that this is the strongest bond. Interestingly, the C_2-C_3 bond strength from F_{22} is roughly equal to the C_3-P bond strength from F_{33}. The phosphorus atom creates a longer bond length by default, but these force constants and the bond lengths show that this molecule is neither acetylenic nor cumulenic. It should be thought of as an intermediate between the two classifications with the C_1-C_2 bond more acetylenic and the rest of the molecule as cumulenic.

In any case, the spectroscopic constants, dipole moment, and vibrational frequencies are given in Table 3 along with the single ^{13}C substituted isotopologues. Phosphorus has only one stable isotope, ^{31}P. C_3P^- is strongly dipolar with a 6.22 D dipole moment as determined from center-of-mass computations. As a result, its rotational intensities should be brighter than the neutral-radical giving further evidence that the anion may be more easily observed in the ISM than the neutral. The rotational constants are not strongly affected by vibrational averaging with B_0 equal to 2798.0 MHz while B_e is only 2.1 MHz greater at 2800.1 MHz. Substitution of the terminal C_1 atom with ^{13}C reduces the rotational constants by 102.0 MHz. Substitution of the other carbon atoms is not as significant. The quartic (D) and sextic (H) distortion constants are exceptionally small for this molecule and may only show up in very high-resolution experiments.

While ground-based telescopes such as the Atacama

Table 1. The C_3P^- Vertical Excitation Energies (in eV), Ground State eBEs[a] (in eV), and Oscillator Strengths.[b]

Transition	pVDZ	apVDZ	dapVDZ	tapVDZ	eBE	f	pVTZ	apVTZ	dapVTZ
$2\ ^1\Sigma^+ \leftarrow 1\ ^1\Sigma^+$	3.52	3.31	3.30	3.30		2×10^{-4}	3.35	3.23	3.24
$1\ ^1\Pi \leftarrow 1\ ^1\Sigma^+$	8.23	5.04	3.98	3.81	3.80	8×10^{-3}	7.03	4.89	4.09

[a]Computed with EOMIP-CCSD/t-aug-cc-pVDZ.
[b]The f values are for EOM-CCSD/d-aug-cc-pVTZ.

Table 2. The CcCR C_3P^- Force Constants Given in mdyn/$\text{Å}^n \cdot \text{rad}^m$)[a].

F_{11}	11.566 227	F_{441}	-0.4428	F_{2222}	219.70	F_{5432}	-0.66	F_{7611}	0.00
F_{21}	0.596 174	F_{442}	-0.5107	F_{3111}	0.15	F_{5433}	0.23	F_{7621}	-1.13
F_{22}	7.708 659	F_{443}	0.0197	F_{3211}	0.12	F_{5444}	0.57	F_{7622}	0.77
F_{31}	-0.380 686	F_{541}	-0.0978	F_{3221}	-0.38	F_{5511}	-0.44	F_{7631}	-0.50
F_{32}	0.689 835	F_{542}	0.0236	F_{3222}	0.66	F_{5521}	0.65	F_{7632}	-0.19
F_{33}	7.655 860	F_{543}	-0.0500	F_{3311}	-0.93	F_{5522}	-0.88	F_{7633}	0.25
F_{44}	0.209 473	F_{551}	-0.0499	F_{3321}	0.31	F_{5531}	0.53	F_{7644}	-2.28
F_{54}	-0.010 817	F_{552}	-0.4968	F_{3322}	0.11	F_{5532}	1.80	F_{7654}	3.47
F_{55}	0.461 190	F_{553}	-0.6287	F_{3331}	1.77	F_{5533}	0.62	F_{7655}	3.32
F_{66}	0.209 484	F_{661}	-0.4424	F_{3332}	-0.64	F_{5544}	0.71	F_{7666}	1.14
F_{76}	-0.010 826	F_{662}	-0.5109	F_{3333}	177.78	F_{5554}	-0.03	F_{7711}	-0.97
F_{77}	0.461 209	F_{663}	0.0190	F_{4411}	1.46	F_{5555}	0.06	F_{7721}	0.54
F_{111}	-71.2065	F_{761}	-0.0952	F_{4421}	-0.19	F_{6611}	1.09	F_{7722}	-1.29
F_{211}	-0.2476	F_{762}	0.0233	F_{4422}	0.61	F_{6621}	-0.42	F_{7731}	0.65
F_{221}	-2.4219	F_{763}	-0.0524	F_{4431}	1.39	F_{6622}	0.69	F_{7732}	1.94
F_{222}	-45.2600	F_{771}	-0.0492	F_{4432}	0.77	F_{6631}	1.53	F_{7733}	-0.61
F_{311}	-0.0455	F_{772}	-0.4972	F_{4433}	0.07	F_{6632}	1.31	F_{7744}	0.03
F_{321}	0.7443	F_{773}	-0.6289	F_{4444}	-0.15	F_{6633}	-0.38	F_{7754}	2.40
F_{322}	-1.7436	F_{1111}	349.14	F_{5411}	-0.05	F_{6644}	1.89	F_{7755}	-0.68
F_{331}	-0.0806	F_{2111}	0.82	F_{5421}	-0.66	F_{6654}	-1.66	F_{7766}	-0.08
F_{332}	-0.8594	F_{2211}	-3.24	F_{5422}	-0.07	F_{6655}	0.71	F_{7776}	0.00
F_{333}	-41.3790	F_{2221}	4.66	F_{5431}	0.64	F_{6666}	-0.25	F_{7777}	-0.76

[a]1 mdyn $= 10^{-8}$ N; The n and m values are exponents that correspond to the number of units from the type of modes present in the specific force constant.

Large Millimeter/submillimeter (ALMA) array are excellent for observing molecular rotational spectra, the growth of space-based or airborne infrared telescopes such as the upcoming James Webb Space Telescope or the Stratospheric Observatory for Infrared Spectroscopy (SOFIA), respectively, has enhanced vibrational spectral analysis for astronomical applications. The vibrational frequencies of C_3P^- are given in the middle of Table 3. The descriptions of the fundamental vibrational modes are not as straightforward as one would assume for a $C_{\infty v}$ molecule. The first two modes are defined here as the symmetric and antisymmetric C−C stretches for the three carbon atom portion of the molecule. The last two modes are the internal and external bends. The former mode is dominated by the C_2 and C_3 atoms moving opposite of one another relative to the central axis. The latter bending vibrational motion is largely described by the C_1 and P atoms moving in concert with one another relative to the central axis. The carbon atom, naturally, covers a greater distance in this mode due to its smaller relative mass, but the two atoms are vibrating in concert.

The CcCR QFF frequencies are not strongly anharmonic. While anharmonic corrections are necessary for accurate descriptions of the vibrational modes, they do not shift as greatly from the harmonic values as is typical. Most of this behavior is probably due to the increased mass of the system largely from the phosphorus atom, but

it is also from the tight bonding present in C_3P^-. Anions are not often thought be tightly bound due to the increased electron-electron repulsion and likely increase in antibonding-character, but C_3P^- appears to be so bound from the data given. In fact, the C−C stretching frequencies in C_3P^- are of the same order as their counterparts in C_3H^+ (Huang, Fortenberry & Lee 2013b). As a result, the vibrational frequencies provided here should be very good representations of physical reality. The frequencies fit SOFIA's range very well, and the ν_1 frequency at 1939.7 cm^{-1} should be very bright since the double-harmonic MP2 intensity is 483 km/mol. It is also worth mentioning that the MP2/6-31+G* harmonic frequency agree well with the CcCR harmonics. MP2 is known to give Pauling points for some properties (Sherrill 2009), but this correlation (< 5.1 cm^{-1}) is largely unprecedented but nicely coincidental for the significantly lower-level MP2 computations.

In the age of ALMA, unidentified lines (or "U-lines") are becoming even more of an issue. Many of these are likely to be caused by rotational transitions of known molecules in vibrationally excited states. As a result, the vibrationally-averaged rotational constants of C_3P^- are also provided at the bottom of Table 3 for each fundamental mode. Vibrationally-excited modes associated with the bending frequencies increase the B values, while the stretching vibrational modes decrease them. ^{13}C substitution largely affects

Table 3. The C_3P^- and Single ^{13}C Isotopologue CcCR Equilibrium and Zero-Point (R_α vibrationally-averaged) Geometries, Rotational Constants, Vibration-Rotation Interaction Constants, Quartic (D) and Sextic (H) Distortion Constants, CCSD(T)/aug-cc-pVTZ Dipole Moment, and Vibrational Frequencies and Intesnities[a].

	C_3P^-	$^{13}CCCP^-$	$C^{13}CCP^-$	$CC^{13}CP^-$	MP2/6-31+G*
$r_0(C_1-C_2)$ (Å)	1.259 055	1.259 200	1.259 058	1.259 065	
$r_0(C_2-C_3)$ (Å)	1.345 935	1.345 909	1.345 920	1.345 906	
$r_0(C_3-P)$ (Å)	1.581 669	1.581 612	1.581 683	1.581 652	
B_0 (MHz)	2798.0	2696.0	2769.6	2798.0	
$\alpha^B 1$ (MHz)	13.3	13.2	12.8	12.9	
$\alpha^B 2$ (MHz)	12.6	11.8	12.4	12.4	
$\alpha^B 3$ (MHz)	4.3	4.0	4.2	4.3	
$\alpha^B 4$ (MHz)	-5.1	-4.9	-4.9	-5.0	
$\alpha^B 5$ (MHz)	-7.9	-7.7	-7.6	-7.8	
$r_e(C_1-C_2)$ (Å)	1.262 119	–	–	–	
$r_e(C_2-C_3)$ (Å)	1.343 872	–	–	–	
$r_e(C_3-P)$ (Å)	1.580 317	–	–	–	
B_e (MHz)	2800.1	2698.0	2771.8	2800.1	
D_e (kHz)	0.202	0.186	0.199	0.202	
H_e (μHz)	1.717	1.654	1.577	1.717	
μ_z[b]	6.22 D	–	–	–	
$\omega_1(\sigma)$ Symm. Carbon Stretch (cm^{-1})	1979.2	1959.0	1930.9	1971.8	1984.3 (483)
$\omega_2(\sigma)$ C_2 Shuttle (cm^{-1})	1481.5	1470.5	1481.2	1439.3	1482.2 (93)
$\omega_3(\sigma)$ C_3-P stretch (cm^{-1})	692.0	681.7	686.6	692.0	689.2 (7)
$\omega_4(\pi)$ Internal Bend (cm^{-1})	479.9	479.4	472.5	469.6	477.0 (4)
$\omega_5(\pi)$ External Bend (cm^{-1})	194.8	192.3	192.4	192.6	195.5 (10)
Harmonic Zero-Point (cm^{-1})	2751.0	2727.3	2714.3	2713.8	2750.4
$\nu_1(\sigma)$ Symm. Carbon Stretch (cm^{-1})	1939.7	1920.0	1913.8	1932.6	
$\nu_2(\sigma)$ C_2 Shuttle (cm^{-1})	1456.5	1446.0	1456.0	1415.5	
$\nu_3(\sigma)$ C_3-P stretch (cm^{-1})	684.0	674.5	678.2	683.9	
$\nu_4(\pi)$ Internal Bend (cm^{-1})	470.8	470.4	463.3	461.3	
$\nu_5(\pi)$ External Bend (cm^{-1})	181.1	178.8	179.0	179.4	
Zero-Point (cm^{-1})	2730.0	2706.7	2698.4	2693.8	
B_1 (MHz)	2784.7	2682.8	2756.8	2785.1	
B_2 (MHz)	2785.4	2684.2	2757.1	2785.6	
B_3 (MHz)	2793.7	2692.0	2765.3	2793.8	
B_4 (MHz)	2803.1	2700.9	2774.5	2803.0	
B_5 (MHz)	2805.9	2703.7	2777.2	2805.8	

[a]Given in parentheses in km/mol beside the MP2/6-31+G* harmonic frequencies.
[b]The coordinates used to generate the Born-Oppenheimer dipole moment component (in Å with the centre-of-mass at the origin) are: C_1, 0.000000, 0.000000, -2.629136; C_2, 0.000000, 0.000000, -1.367016; C_3, 0.000000, 0.000000, -0.023143; P, 0.000000, 0.000000, 1.557174

the rotational constants in similar ways between isotopologues as it does for B_0. Finally, a limited line list for the $J \leqslant 9$ rotational transitions of the $\nu = 0$ and $\nu_5 = 1$ vibrational states is provided in Table 4 in order assist with further analysis. Previous work (Fortenberry et al. 2013a) has shown that the rotational constants are probably within 10 MHz of experiment putting the anticipated rotational constants within $2J \times 10$ MHz for each line predicted in Table 4, and the relative intensities between the rotational transitions should be very close to experiment.

4 CONCLUSIONS

The electronic properties of C_3P^- are in line with those for the known interstellar anions indicating that it may be a viable molecule waiting to be detected in the ISM. Attachment of an additional electron to the corresponding neutral-radical via the anion's dipole-bound excited state is a likely creation mechanism for this anion. Additionally, C_3P^- possesses not only a valence ground electronic state but also a valence excited state. The second excited state should increase the molecule's lifetime. Since $[C_6H^-]/[C_6H] > 1$ (Agúndez et al. 2008), it is likely that $[C_3P^-]/[C_3P]$ is as well since both radicals possess strongly dipolar ground electronic states available for binding the extra electron leading to the observed valence anion. The valence excited state in C_3P^- should boost the $[C_3P^-]/[C_3P]$ ratio further due to the enhanced stability in the phosphorus anion. Furthermore, the anion's dipole moment is greater than that in the neutral-radical enhancing the anion's rotational signal. As a result, C_3P^- may be a better candidate for detection than C_3P.

In order to assist in potential searches, the spectroscopic constants and vibrational frequencies for C_3P^- are provided in this work. Ground state C_3P^- is tightly bound, especially considering that it is an anion, and not strongly anharmonic. Hence, the CcCR approach utilized previously with

Table 4. The C_3P^- 150 K CcCR $\nu = 0$ and $\nu_5 = 1$ Rotational Limited Line List with $\Delta E_{J+1 \to J}, J \leqslant 9$ with Frequencies in MHz and Intensities in MHz per molecule.

Mode	J+1	J	Frequency	150K Intensity
$\nu = 0$	1	0	5596.0	0.011
$\nu = 0$	2	1	11 192.0	0.042
$\nu = 0$	3	2	16 788.0	0.093
$\nu = 0$	4	3	22 384.0	0.164
$\nu = 0$	5	4	27 980.0	0.257
$\nu = 0$	6	5	33 575.9	0.367
$\nu = 0$	7	6	39 171.8	0.492
$\nu = 0$	8	7	44 767.7	0.628
$\nu = 0$	9	8	50 363.5	0.792
$\nu = 0$	10	9	55 959.3	0.961
$\nu_5 = 1$	1	0	5611.8	0.002
$\nu_5 = 1$	2	1	11 223.6	0.006
$\nu_5 = 1$	3	2	16 835.4	0.014
$\nu_5 = 1$	4	3	22 447.2	0.025
$\nu_5 = 1$	5	4	28 058.9	0.040
$\nu_5 = 1$	6	5	33 670.7	0.057
$\nu_5 = 1$	7	6	39 282.4	0.076
$\nu_5 = 1$	8	7	44 894.0	0.097
$\nu_5 = 1$	9	8	50 505.7	0.122
$\nu_5 = 1$	10	9	56 117.2	0.148

very good results should be similarly accurate in this system. The ν_1 C$-$C stretch is very bright, and the vibration-rotation interaction constants are small. In summary, C_3P^- is an excellent interstellar molecular candidate, and the data provided in this work should assist in spectral searches for this anion whether in the laboratory or in the ISM.

5   ACKNOWLEDGEMENTS

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